

Probing uranyl peroxide materials U₆₀ and sStudtite using *in situ* electrochemical XAS methods

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Introduction

The electrochemical nature of the uranium-60 nanocluster (U₆₀), a spherical cluster of uranyl polyhedra, has yet to be fully characterized since its first synthesis in 2005 [1]. While our initial studies on U₆₀ and its naturally-occurring analog, studtite, focus on monitoring the redox behavior in differing solutions and concentrations in order to characterize redox switching in both compounds (U⁶⁺ to U⁵⁺ and U⁴⁺), we have recently studied local structural changes as a function of redox state [2].

Purpose

Our hypothesis is that we can measure and calculate the thermodynamics and redox potential of the redox switching, including its kinetics and reversibility (*i.e.*, switching within the cluster without destroying it) in U₆₀ clusters and studtite as a function of pH, solution chemistry, and pe/Eh. In addition, changes in the kinetics of growth, structural, and electronic changes are monitored by a combination of electrochemical X-ray Absorption Spectroscopy (XAS) and computational treatment of activated complexes. Synchrotron XANES/EXAFS allows us to determine the oxidation state of U as a function of the applied potential and elucidate the structure and changes on U₆₀ clusters found on the electrode.

Results

Electrochemical results describe the proton-coupled nature and similarity of U₆₀ and studtite redox behavior (peaks within 0.1V of each other) in addition to the alteration of (UO₂)²⁺ in the presence of uranyl peroxides. *In situ* electrochemical synchrotron XAS results support our initial peak characterizations and purity of our synthetic samples.

Experiments induce potential to oxidize/reduce samples, identifying them in reference to standard electrode potentials and investigating redox potentials in varied conditions. These results can describe how actinide species in environmental conditions interact with mineral surfaces and surface-mediated redox processes. Such information is essential to any experiment concerning sorption, precipitation, diffusion, surface complexation, and solid solution formation.

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[1] Sigmon *et al.* (2009) *JACS* **131**, 16648-49. [2] Gebarski & Becker (in submission) *GCA*.